INTERACTION BETWEEN CLAYS AND ORGANIC COMPOUNDS IN SOILS. PART II. ADSORPTION OF SOIL ORGANIC COMPOUNDS AND ITS EFFECT ON SOIL PROPERTIES

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ADSORPTION OF SOIL ORGANIC COMPOUNDS

Chemical Nature of Soil Organic Compounds

A brief account of the constitution of the components of soil organic matter is included here since it is necessary to any appreciation of their adsorption behaviour. The recent advances in the understanding of adsorption of polymers have shown the importance of size, shape and flexibility of polymer molecules in this respect. These properties, as well as the chemical constitution may differ for organic materials extracted from different soils, and may also differ for materials extracted from any one soil by different techniques. Nevertheless the limited data at present available provide a reasonably coherent picture, although undoubtedly this will be somewhat modified as more data are obtained.

A wide range of organic compounds occurs in soils. The chemical constitution of many of these remains unknown, but some progress in the determination of their constitution has been made in the last decade (cf. Scheffer & Ulrich, 1960; Dubach *et al*, 1964; Kononova, 1965). Once the non-humified organic materials have been separated the principal remaining components are the mixtures known as humic acid (the part soluble in alkali and precipitated by acids) and fulvic acid (the part soluble in alkali and not precipitated by acids) and the humins (the part not extracted by alkali).

(i) Humic acids.

These are composed of amino acids and phenolic compounds, combined in a manner as yet unknown, to form a group of high-molecular-weight polymers. Studies of these compounds with the ultracentrifuge (Stevenson, Van Winkle & Martin, 1953; Piret *et al*, 1960; Schluter, 1959) indicate that most of the materials present have molecular weights in the range 20,000-50,000, and there may be a smaller group with molecular weights over 100,000. Fractionation of humic acids by gel filtration on Sephadex (Posner, 1963; Mehta, Dubach & Deuel, 1963) also indicates that molecular weights lie within these ranges although humic acids separated from the B horizon of podzols may give lower values. Other techniques for molecular-weight determination have been used, but are less satisfactory. Electron micrographs (Flaig & Beutelspacher, 1951; Beutelspacher, 1955; Visser, 1963) indicate that dried humic acids are composed of approximately spherical particles. The low viscosities of their aqueous solutions (Scheele, 1937; Beutelspacher, 1952; Flaig, Scheffer & Klamroth, 1955; Piret *et al*, 1960) suggest that this shape persists in an aqueous environment, and the ultracentrifuge data also accord with this. Furthermore the molecules must be relatively rigid, since as the pH is raised and the molecules become more highly charged, little change in viscosity occurs. Flexible polymers are extended as the charge on the molecule increases (cf. Tanford, 1961). Detailed analysis of the titration curves of humic acids (Posner, 1964) shows that they are unlike those of linear polyelectrolytes. Titration curves also show that large numbers of acidic groups are present, about half of which are negatively charged at pH 5-7 (Scheffer & Ulrich, 1960).

(ii) Fulvic acids.

These are a more heterogeneous group. Fractionation by chromatographic methods (Forsyth, 1947; Dragunov, 1951; Schlichting, 1953; Dubach *et al*, 1955) has shown that the principal components are a group of phenolic materials probably similar to humic acids but of lower molecular weight (Kononova, 1965) and a group of polysaccharides. Other materials are also present. Forsyth (1950) isolated only a small fraction of the soil organic matter in the form of polysaccharides, but after elution much polysaccharide material remains on the charcoal pad used for the separation (Swincer & Greenland, unpublished). If the fulvic acid is fractionated with Sephadex (Roulet *et al*, 1963; Barker *et al*, 1964) up to 30% of the fulvic-acid carbon can be isolated as polysaccharide materials. This accords with studies of the total carbohydrate contents of soils that indicate that 5-30% of the soil carbon is present in this form (Mehta, Dubach & Deuel, 1961). These polysaccharides are

themselves mixtures of several individual polymers. Only partial separation of these has been achieved (Müller, Mehta & Deuel, 1960; Barker *et al*, 1964). The high viscosities of their solutions indicate that they are large, linear and flexible molecules. Their behaviour in the ultracentrifuge (Ogston, 1958; Mortensen, 1960) supports this; the mean molecular weights obtained were 120,000 and 400,000. Uronic groups are usually present with the polysaccharides (Mehta, Dubach & Deuel, 1961), but the proportion of carboxyl groups is much less than with humic acids, and furthermore may be restricted to only certain of the polysaccharides that are present (Barker *et al*, 1964).

(iii) Humins.

These are the organic compounds irreversibly bound to the mineral part of the soil, and may also include some other material. Kononova (1965) cites unpublished work of Khan which indicates that humins have a slightly lower carbon content than the humic acids of the whole soil, although they are otherwise similar. The lower carbon content suggests that the proportion of aromatic carbon present is less than in humic acids. No data are available concerning the detailed constitution or physico-chemical properties of the humins.

Adsorption Studies with Soil Organic Compounds

If, as seems probable, humic acids have molecules which are relatively compact, negatively charged spheres, it is unlikely that they will be adsorbed by physical adsorption forces alone. In fact it is expected that they will be repelled from the largely negatively charged clay surfaces. However ultrasonic dispersion in heavy liquids separates only a small proportion of the humic acids from the mineral part of the soil (Greenland & Ford, 1964). Presumably they are held by positive sites on the clay particles, or on hydroxy-aluminium oligomers or polymers, or by 'bridge linkages' involving polyvalent cations. There is considerable experimental evidence to support this interpretation. X-ray studies have shown that humic acids do not penetrate the interlamellar regions of montmorillonite (Sedletsky & Tatarinova, 1941; Jung, 1943; Evans & Russell, 1959) although Kononova (1965) states that Khan has observed such penetration. Quantitative studies with humic acids have also shown that there is no adsorption by sodium montmorillonite (Evans & Russell, 1959; Martin & Reeve, 1960) unless the clay is first made acid and aluminium enters the exchange sites. Flaig & Beutelspacher (1951) consider that their electron micrographs of mixtures of montmorillonite and humic acid show that an association between humic acids and montmorillonite occurs only through the intermediary of aluminium (or iron) oxides. Other studies of the adsorption of humic acids have shown that in otherwise similar conditions larger amounts are adsorbed when iron and aluminium are present on the exchange sites (Sen, 1960; Kobo & Fujisawa, 1963). Aleksandrova (1954), Aleksandrova & Nad (1958),

Martin & Reeve (1960), Martin (1960), Evans & Russell (1959) and Schnitzer & Skinner (1964) have shown that humic and fulvic acids are readily adsorbed by freshly synthesised iron and aluminium oxides. Aleksandrova & Nad (1958) note that old, crystalline forms of the oxides are less reactive than freshly precipitated material. These observations support Flaig & Beutelspacher's suggestion that oxides may act as bridges linking the humic acids to clay lattices. The exact manner in which the humic materials are bonded to the aluminium or iron oxide is not established; ionic interaction, coordination or chelation or all three could be involved. Aleksandrova & Nad (1958) point out that humic acids are precipitated when iron and aluminium replace hydrogen ions, and surface precipitation rather than adsorption may occur. Drying of the clay-organic complex leads to the formation of a condensed surface film not readily removed. No systematic study of the effects of drying on the removal of humic materials from clays seems to have been made, but this hypothesis would explain the presence of very difficultly extractable humic materials in the humin fraction, and merits further investigation. The general observation that larger amounts of humic acids are adsorbed by clay minerals in the presence of polyvalent cations (Meyer, 1935; Myers, 1937; Jung, 1943; Khan, 1950; Evans & Russell, 1959) is probably to be explained in terms of formation of bridge linkages, but in addition the same variety of mechanisms as account for the adsorption by iron and aluminium oxides may be involved.

The electron micrographs of Beutelspacher (1955) suggest that humic acids are attached only to the edges of kaolinite crystals. Since these edges can be positively charged a direct association between the carboxylate groups of the acid and the edges of the clay is possible. Such an association seems probable, and adsorption of other organic polymers (see Part I) supports its occurrence, but no direct evidence for this seems to have been presented.

No detailed studies of the adsorption of polysaccharide materials separated from soils have yet been reported. Beutelspacher (1955) obtained electron micrographs which showed that mucilagenous gums from worm guts formed complexes with kaolinite crystals in which the gum was spread along the surface of the clay. Dubach *et al* (1955) and Greenland (1956) showed that soil polysaccharides were readily adsorbed in large amounts by montmorillonite, and Greenland also observed that, in contrast to humic acids, the soil polysaccharide readily formed an interlamellar complex with montmorillonite. This strong adsorption is the type of behaviour that would be predicted for large, linear, uncharged molecules. More detailed studies of the adsorption of polysaccharides separated from soils are obviously needed to clarify their significance in the interaction between clays and organic compounds in soils.

Separation of Organic Compounds from Soils and Clays

The separation of organic materials from soils and clays has been much more extensively studied than the processes which follow the addition of such compounds to clays. Most of the material extracted by density-difference methods is only partially decomposed. Thus most of the humified material must be attached to denser inorganic colloids. The principal mechanisms by which the organic colloids are held in presence of water are by ionic attachments to oppositely charged material, including in this the 'bridge' links due to ions of multiple charge that can link similarly charged colloids, and, for large flexible molecules, multiple van der Waals forces and entropy effects. To extract the organic materials from the inorganic it is necessary to add a solution in which the organic, but not the inorganic, colloids will dissolve or peptize, and which will detach them from the inorganic colloids.

The organic colloids are mostly soluble or peptizable as the salts of monovalent cations, with the exception, for humic acids, of hydrogen. Sodium or ammonium chloride can therefore be used to extract organic materials (Tyulin, 1938; Atkinson & Turner, 1944; Nad, 1957; Brydon & Sowden, 1959) but the extraction is far from complete, since all that is removed is uncombined material or material linked to the clay particles only by a multiply charged ion such as Ca^{++}. If the soil is treated with the sodium or ammonium salt of an anion such as pyrophosphate, oxalate, fluoride or ethylene diamine tetra-acetate (EDTA) cations such as calcium, iron and aluminium, which render the organic materials insoluble and link them to the clay, combine with the added anions, so that organic materials held in this way are released (Simon, 1929; Chaminade, 1946; Bremner & Lees, 1949; Bremner *et al*, 1946; Hamy & Leroy, 1952; Maes & de Leenheer, 1954; Martin & Reeve, 1957; Evans, 1959; Aleksandrova, 1960a, b; Dubach, Mehta & Deuel, 1961). These methods usually release about 10% to 30% of the soil carbon (see e.g. Bremner & Lees, 1949; Evans, 1959). Humic materials attached to positive sites on oxides or at the edges of clay lattices may also be partly replaced, since the anions will compete for the positive sites. Where the ionic bond is supplemented by physical adsorption forces between other parts of the organic molecule and the clays, extraction may be incomplete. Martin & Reeve (1957) examined the extraction of organic matter by reagents forming progressively stronger complexes with Fe and Al, but concluded that no precise information on the strengths of retention of organic matter could be obtained since the factors controlling dispersion of the released materials are as important as the breaking of metal-organic matter bonds.

Larger amounts of humic material are usually extracted by sodium hydroxide solutions. In such solutions the organic colloids are strongly negatively charged and so disperse readily, and the isoelectric points of the oxides and edge groups of clay minerals are exceeded so that retention by positive charges on the inorganic colloids is no longer possible. But probably the most important reason why more humic acid is released by alkaline extraction is that Al and Fe are displaced from the humic acids more efficiently by the alkali, and not that the humic acids are more effectively displaced from the inorganic colloids. It is also possible that the organic polymers are partially hydrolysed and the smaller molecular fragments are peptized since they are now more weakly adsorbed.

If the free organic materials have been removed initially by a density method the residual materials are those held by multiple van der Waals forces and the entropy effect, and perhaps those precipitated on the clay and rendered insoluble by drying. Emerson (1956) has shown that whereas sodium pyrophosphate or hydroxide will displace adsorbed polyanions from clays, they will not displace an uncharged polymer such as polyvinyl alcohol. Uncharged soil polysaccharides might therefore be expected to be concentrated in the humin fraction, but there are no data to substantiate this hypothesis.

Studies of Clay-Organic Interactions by light Microscopy

Kubiena (1964) considers that the processes involved in the formation of clay-humus aggregates in soils are only fully seen when soils are studied with the light microscope. The processes so far considered in this review take place at the molecular level, and while the electron microscope affords some useful supplementary information, the light microscope provides no information about such processes. It does provide information about entanglement of soil particles by, for example, fungal hyphae (Hubbel & Chapman, 1946). The type of aggregation produced in this way may be important in morphological studies of soils and to agricultural practice, since it will in part determine the nature and stability of the coarse pores. Jongerius and Pons (1962) have discussed the different types of clay-organic mixtures that are produced when different groups of soil animals decompose plant remains. However at the stage at which interactions other than mechanical entanglement become important the structures pass into the condition referred to as 'amorphous' by the light microscopists.

The high concentrations of organic material in the gut of soil animals may be important in promoting the physico-chemical interactions between clays and organic compounds. Meyer (1941, 1943) suggested that the rather weak adsorption of separated humic materials and the firm retention of much of the natural humic material might be reconciled if the adsorption took place during synthesis of humic acids and while clay and organic materials were being thoroughly mixed in the guts of worms. More recently Schulz (1958) has obtained photomicrographs of worm casts which indicate that condensation of humic acids is promoted there by iron oxides, and Jeanson-Luusinang (1960) has found that a larger proportion of organic carbon is combined with the inorganic colloids in worm casts

than in the soil as a whole. This probably reflects the fact that the organic matter is more completely humified by bacteria in the gut of earthworms, than when it is distributed throughout the soil. Swaby (1950) observed that the increased stability of aggregates of soil in worm casts was due to the greater proportion of organic matter converted by slime-producing bacteria.

EFFECT OF THE INTERACTION BETWEEN INORGANIC AND ORGANIC COMPOUNDS ON SOIL PROPERTIES

Adsorption of organic materials by clays changes the surface presented to the surrounding medium, and thereby their interaction with water and electrolytes. The formation of interparticle bonds will also modify their swelling properties and the strength of aggregates, since the possibility of positional adjustment is restricted.

The significance of the location of an organic molecule within a soil aggregate has received as yet relatively little attention, though it may well be very important in determining the extent to which the physico-chemical, physical and biological properties of the soil are modified by the clay-organic inter-action. Quirk & Panabokke (1962) and Williams (1965) have obtained evidence that natural organic materials lining relatively coarse pores (of the order 50 μ e.s.d.) exert the most important effects on the strength of aggregates. Emerson (1959) presented a model of the structure of soil crumbs, in which he indicated that the organic polymers were excluded from the internal surfaces of clay domains. It is probable that this is correct, but as yet there is no satisfactory evidence to show what proportion of clay surfaces are covered by organic materials. Williams (1965) has recently shown that when an aggregate is placed in contact with a solution of a strongly adsorbed polymer such as polyvinyl alcohol, the polymer penetrates only the periphery of the aggregate. Thus even in surface soils there may be as many clay surfaces free of organic materials, as there are surfaces on which organic matter is adsorbed. As Griffiths (1965) has stated the question of the distribution of organic polymers within the soil merits much further attention.

Some qualitative ideas regarding the effects of adsorbed organic materials on the properties of soils can be obtained from the changes which occur when organic compounds are added to clays, and when organic materials are extracted from or destroyed in soils. Correlations between the amounts of total organic matter or components of the organic fraction and certain soil properties have also been used to provide information regarding the effect of the organic materials.

Physico-chemical properties.

(i) Effects of adsorption of organic cations.

Organic cations are less strongly hydrated than inorganic cations. Consequently when inorganic cations are displaced from clay surfaces the affinity of the clay for water is reduced (Hendricks, 1941;

Kurilenko & Mikhalyuk, 1958; Emerson, 1963; Greenland, Quirk & Theng, 1964). The decrease in the tendency of the clay to adsorb water is more pronounced with alkylamines containing more than six carbon atoms. This indicates that the effect is due not only to the lower hydration energy of the organic cation but also to the displacement of water from the clay surface by the hydrophobic alkyl groups. "Waterproofing" of clays by adsorption of alkylammonium compounds has been rather extensively studied in relation to its potential use in the stabilization of soils for engineering purposes (Clare, 1947; Grossi & Woolsey, 1955; Hoover & Davidson, 1956; Chakravarti, 1956).

A similar mechanism may account for the non-wetting of certain sandy soils. Such soils are fairly widespread, and the reason for their non-wetting seems to be that the sand grains are coated with hydrophobic organic materials (Thornton, Cowie & McDonald, 1956; Bond, 1964).

It has also been shown that treatment of soils with amphipathic compounds will decrease water losses (Bowers & Hanks, 1961; Olsen *et al*, 1964; Hemwall & Bozer, 1964). The latter authors present evidence which indicates that limited soil regions are rendered hydrophobic, and the reduction of water loss is due to the fact that water moves much less readily through these regions.

Adsorption of certain organic compounds causes increased swelling of some clays. Thus butyl-, propyl- and amyl-ammonium vermiculites may show extensive swelling in water (Garrett & Walker, 1962). The effect is probably due to the formation of "iceberg" or clathrate structures on the surface of the mineral. Partial displacement of calcium ions from montmorillonite by small alkylammonium ions may also lead to extensive swelling, in this instance probably due to the disruption of water structures between the adjacent lamellae (Greenland, Quirk & Theng, 1964). In both instances the effect seems to be rather critically dependent on the surface density of charge of the mineral. Increased swelling is also induced by amino acids when adsorbed (Barshad, 1952; Walker & Garrett, 1961; Greenland, Laby & Quirk, 1962). This is due to the increase in dielectric constant of the medium separating the lamellae.

Where adsorption of an organic compound increases the tendency of the clay to swell in water, the residual inorganic cations should be more readily exchangeable. This has not been established, but it has been shown that displacement of small amino-acid cations from vermiculite or montmorillonite is difficult only when they cause a partial closure of the lamellae (Mortland, 1961; Greenland, Laby & Quirk, 1965). When alkylammonium ions which decrease the swelling of clays are adsorbed not all the inorganic cations can be displaced (Hendricks, 1941; Ensminger & Gieseking, 1941; Mukherjee, 1954; Morel & Henin, 1956; Weiss, 1959; Kurilenko & Mikhalyuk, 1959; Greenland & Quirk, 1962). The mechanism by which this restriction in the freedom of the inorganic cations occurs is not entirely clear. Hendricks' (1941) original

concept of a steric covering of the inorganic ions, perhaps best supported by the data of Weiss (1959), has been widely accepted. For montmorillonite the decreased interlamellar distances may also restrict movement. However the adsorption of a layer of uncharged polyvinyl alcohol 10A thick on all surfaces of sodium montmorillonite produced virtually no decrease in the cation-exchange capacity (unpublished data of Luxmoore & Greenland).

(ii) Effects of adsorption of organic anions.

Calgon (sodium polymetaphosphate) is well known as a clay dispersant. It is thought to act by blocking the positive sites on the clay that enable electrostatic bonds to be formed between the edges and faces of clay particles and cause "cardhouse" floccules to form, and by complexing polyvalent cations which produce flocculation of the clay. Many organic anions added to clay suspensions in small amounts have a similar effect. Van Olphen (1963) discusses the use of tannates as dispersants, and oxalates (Folks & Riecken, 1956), polyphenols (Bloomfield, 1957), polyuronides (Schnitzer & De Long, 1955), fulvic and humic acids (Wurman, Whiteside & Mortland, 1959; Martin & Reeve, 1960), root exudates (D'Hoore & Fripiat, 1948) and leaf leachates (Bloomfield, 1954) have all been shown to promote the dispersion of clays. Addition of the anion in sufficient amount may lead to flocculation, in the same way as the addition of any other salt. The dispersing effect of the anion can also be masked if interparticle bonds are formed (see below).

In a number of instances it has been reported that after adsorption of an anionic organic electrolyte the total negative charge (cation exchange capacity) is less than the sum of the negative charges of clay and organic compound (Myers, 1937; McLean, 1952; Archibald & Erikson, 1955; Gaur, 1964; Sen, 1964; Helling, Chesters & Carey, 1964). This has mostly been attributed to the fact that the carboxyl groups become bonded to the clay. However, interaction may take place through physical adsorption forces involving uncharged parts of the organic molecule. This would conform with observations of Sakun (1942), Tschapek & Sakun (1944) and Aleksandrova & Nad (1958) that there was no loss of cation exchange capacity when humic acid and clay suspensions were mixed. The subject is complex and requires more detailed analysis than it has yet received.

The adsorption of fulvic acid (Leaver & Russell, 1957) and humic acid (Okuda & Hori, 1957) reduced the sorption capacity of the soil for phosphate. The sorption of other nutrient anions is probably also affected, but again the phenomenon has been little studied.

(iii) Formation of interparticle bonds.

In spite of the dispersing action of organic anions, many long-chain organic polyanions are excellent flocculators of clays (Ruehrwein & Ward, 1952; Michaels, 1954; Hagin & Bodman, 1954; Michaels & Morelos, 1955; Beutelspacher, 1955;

Bergmann & Fiedler, 1956; Packter, 1957; Holmes & Toth, 1957; Fiedler & Torstensson, 1957; Warkentin & Miller, 1958; McCarty & Olson, 1959; La Mer & Smellie, 1960; Maslenkova, 1961; La Mer & Healy, 1963). Flocculation is due to formation of interparticle bonds. Negatively charged polymers which are extended in solution and do not collapse to negatively charged surfaces are particularly effective flocculants in this way. Uncharged compounds are generally less effective, unless they are very large (such as the dextrans studied by Novak, Witt & Hiler, 1955). They will however form interparticle bonds if they are added to clay systems where the particles are already in close proximity (Greenland, 1963). Thus poor flocculators such as polyvinyl alcohol and some carboxymethylcelluloses are nevertheless very effective in the stabilization of soil aggregates (Emerson, 1956; Fiedler & Torstensson, 1957; Davis & Heald, 1964; Williams, 1965).

The mode of action of charged and uncharged polymers in stabilizing soil aggregates is rather different; polyanions become attached to several particles, but only a few segments of the polymer are bonded to each particle; flexible uncharged polymers spread over the surfaces with which they come into contact, and if such surfaces are already adjacent, they form many bonds to each surface (Fischer & Rentschler, 1957). The action of negatively charged polymers may be likened to the formation of "strings of beads" and of uncharged polymers to the spreading of "coats of paint" around groups of particles already in proximity (Greenland, 1963).

Physical properties.

(i) Water-stable aggregation.

It is well known that there is a general relation between the physical properties of a soil and the amount of organic matter it contains. This is supported by the correlations between such properties as water-stable aggregation and carbon content, reported by Baver (1935), Clarke & Marshall (1947), Rennie, Truog & Allen (1954), Heinonen (1955), and Chesters, Attoe & Allen (1957). The correlations are seldom very close, but this is not surprising since total organic carbon may not be correlated with the carbon content of those organic compounds which influence the physical properties of the soil (Kullmann & Koepke, 1961; Greenland, Lindstrom & Quirk, 1962). Furthermore soil aggregates can be stabilized by aluminium oxides and calcium carbonate as well as organic materials (Greenland, Lindstrom & Quirk, 1962; Deshpande, Greenland & Quirk, 1964), so that the influence of the organic material is not necessarily apparent. More direct evidence of the importance of the clay-organic interaction to the physical properties of soils is provided by observations of the effects of addition of organic material to soil. This evidence has been reviewed by Martin *et al* (1955). The greatest effects are produced by those organic compounds which influence the physico-chemical properties of clays.

Martin *et al* (1955) discuss the importance of preventing the soil slumping into a mass containing only very fine pores, in which air and water movement would be very slow. It is possible that humic materials, as well as undecomposed organic materials may be important in this respect. On the other hand polysaccharide materials, particularly microbially produced polysaccharides, are very effective in increasing the stability of aggregates when added to soils (Martin, 1946; Geoghegan & Brian, 1948; Swaby, 1949; Geoghegan, 1950; Quastel, 1952; Rennie, Truog & Allen, 1954; Whistler & Kirby, 1956; Bernier, 1958; Clapp, Davis & Waugaman, 1962). Humic materials are less effective (Swaby, 1949; Whistler & Kirby, 1956). This accords with their adsorption behaviour and influence on physico-chemical properties discussed earlier.

These experiments, in which organic materials have been added to soils, do not establish that the same mechanisms of aggregate stabilization occur in natural aggregates. However, the loss of stability brought about by treatment of natural aggregates with dilute periodate, which oxidises the polysaccharides but has little effect on other materials, confirms that in many soils polysaccharides play the most important role (Greenland, Lindstrom & Quirk, 1962; Harris *et al*, 1963; Clapp & Emerson, 1965).

It is probable that this stabilization is effected by the formation of interparticle bonds. Whether the polysaccharides act by the "string-of-beads" or "coat-of-paint" mechanism must remain an open question until more is known of their constitution. They contain a significant number of ionic groups, but whether both polyuronides and uncharged polysaccharides are present is not known. It is quite possible that only certain components of the soil polysaccharides are active in aggregate stabilization. It is known that different microbially produced materials have very different effects (Martin *et al*, 1955; Clapp, Davis & Waugaman, 1962; Harris *et al*, 1964).

Other organic materials in addition to polysaccharides increase the stability of soil aggregates, but the nature of these remains uncertain. Mehta *et al* (1960) suggested that these were humic materials. Greenland, Lindstrom & Quirk (1961) suggested fungal hyphae and mycelia and Griffiths (1965) has put forward the possibility that lipids are responsible. As yet it is not possible to decide between these possibilities.

(ii) Surface area.

The non-humified organic materials in soils have a small external area and large internal area, in common with other cellulosic materials. Thus to obtain information about the effect of adsorbed organic compounds on the accessible surface of the clay this material should first be removed. When this is done it is found that removal of the remainder of the organic matter leads to an increase in the specific surface area (Burford *et al*, 1964; Mitchell, Farmer & McHardy, 1964). Kuron, Preusse &

Föhrenbacher (1961) noted an increase in adsorption of ethylene glycol after peroxidation of a number of soils, and Aleksandrova & Nad (1958) reported that peroxidation of a clay-organic complex gave rise to increased water adsorption. Thus the organic materials must fill or block pores which are made available by their removal.

(iii) Porosity, permeability and other physical properties.

Water-stable aggregation influences plant growth by virtue of its relationship to the maintenance of a porosity suitable for air, water or root movement. Unless a large proportion of the soil is contained in aggregates of mean diameter 0.5-2 mm, the soil will contain few coarse pores through which air and water movement can occur. The effect of adding organic materials on properties such as permeability and water retention has been measured by Hedrick & Mowry (1952), Peters, Hagan & Bodman (1953), Hagin & Bodman (1954), Mortensen & Martin (1954), Taylor & Baldridge (1954), Haise, Jensen & Alessi (1955), Jamison & Kroth (1958), Pugh, Vomocil & Nielsen (1960) and Gussak (1961). Marked improvements in permeability, not necessarily accompanied by changes in water retention, have been found. The organic materials generally maintain a larger proportion of coarse pores in the soil by holding the soil aggregates intact and so preventing the filling of the pores by dispersed clay materials. It has been suggested that natural organic materials prevent slaking of soil aggregates by providing a hydrophobic coating to some pores, as well as by interparticle bonding (Henin, 1948; Emerson, 1954). A hydrophobic coating leads to a finite contact angle between water and soil surfaces, and a slower rate of wetting. Robinson & Page (1950), however, found that differences in amounts of organic matter in the soil did not lead to measurable contact angle differences and Quirk & Panabokke (1962) have also observed this. Quirk & Panabokke consider that differences in stability and rate of wetting due to the organic materials are associated with their disposition in the aggregates. By lining and strengthening coarse pores "incipient failure" is prevented, and rapid-wetting planes are not formed. This accords with the effects of the organic materials on aggregate stability, and explains very adequately the observations of increased permeability and diffusion rates.

Positive contact angles for water on soil may well occur, but they seem to be restricted to the special conditions of very sandy soils, in which a rather particular type of organic material develops (Bond, 1964).

The addition of organic materials to soils has been observed to produce an increase in the mechanical strength of individual aggregates (Homrighausen, 1957; Quirk & Panabokke, 1962; Modina, 1962; Williams, 1965), although not necessarily of the soil as a whole (Jamison, 1954; Allison, 1956; Allison & Moore, 1956; Pugh, Vomocil & Nielsen, 1960). This indicates that interparticle bridging is possible within aggregates,

but the extent to which this is possible between aggregates is insufficient to enable significant increases in the bulk strength of the soil to occur.

Biological properties.

The interaction between clays and organic compounds has an indirect, but nevertheless very important, influence on the biological properties of soils through its effect on the physical condition of the soil; it has also a direct effect on the availability of organic materials to soil animals and microbes. The hypothesis that proteins constitute a large proportion of soil organic matter was untenable unless some mechanism could account for the fact that they were not destroyed by soil organisms. One such suggested mechanism was that they are protected by adsorption on and in clay minerals (Ensminger & Gieseking, 1939). This focussed attention on the protective action of clay minerals. In fact, both protection and stimulation can occur. The literature relating to both effects has been reviewed by Estermann & McLaren (1959).

Protection is generally associated with interlamellar adsorption in expanding lattice clays such as montmorillonite (Ensminger & Gieseking, 1942; Bower, 1949; Pinck, Dyal & Allison, 1954; Birch & Friend, 1956; Lynch & Cotnoir, 1956; Estermann, Peterson & McLaren, 1959). Proteins are not necessarily inaccessible to enzyme attack when adsorbed in the interlamellar regions of clays (Estermann, Peterson & McLaren, 1959), although the rate of attack is decreased and may be greatly decreased if the protein when adsorbed spreads on the surface to form a monolayer 5A thick (Pinck, Dyal & Allison, 1954). It·is probable that the change in configuration of the adsorbed materials and inaccessibility of specific groups, as well as adsorption of the attacking enzyme (Mortland & Gieseking, 1952) are involved. It seems unlikely that interlamellar adsorption is important in the preservation of soil organic matter even in those soils containing expanding-lattice clays since the existence of natural interlamellar organic complexes in soils has not been reported. This may be because they have not been sought.

Adsorption on external surfaces of clays seems to afford some degree of protection for organic materials (Ensminger & Gieseking, 1942; Mortland & Gieseking, 1952; Birch & Friend, 1956; Lynch & Cotnoir, 1956). On a weight basis protection is generally much less than that afforded by montmorillonite although it could be more closely comparable on the basis of protection per unit area of surface. However, McLaren & Estermann (1956) observed that the rate at which proteins adsorbed as monolayers on kaolinite could be attacked by chymotrypsin was little different from that for the non-adsorbed material.

A decrease in the rate of decomposition of plant material when clay is added to bacterial cultures or sand or soil is sometimes attributed to adsorption effects (e.g. Pinck & Allison, 1951). It is possible however for the differences to be due to changes in physical conditions, such as aeration, and pore structure. As Rovira & Greacen (1958) have pointed out, organic matter contained in pores smaller than about one micron $(10^{-4}cm)$ diameter may be inaccessible to bacteria, and thereby protected, although it is not adsorbed. Protection against extracellular enzymes would then depend on adsorption of the enzyme. The significance of accessibility factors will be much less in soils subject to considerable working by the soil fauna.

Accessibility effects may account for the high levels of organic matter in clay soils. The particularly high levels found in allophane soils could be associated with adsorption, as Broadbent, Jackman & McNicoll (1964) have suggested, but it is also possible that the stability is associated with the large amount of aluminium bonded by the organic matter. The levels of organic matter in many latosols are greater than predicted from climatic relationships derived for temperate soils (Jenny, 1961), and this may again be due to a stabilizing effect of iron and aluminium oxides. Krasnozems (at least the Australian variety) are another group of soils of exceptionally high organic content, and also have high contents of "free" iron and aluminium oxides. Some type of mineral-organic association is very probably involved, but its nature is at present uncertain.

As mentioned above adsorption can increase the rate of bacterial activity, as well as depress it. Thus Estermann and McLaren (1959) observed a stimulation of the rate of breakdown of proteins adsorbed on kaolinite, and noted several other instances in which colloids have been found to increase the rates of bacterial reactions. They suggest that stimulation can be due to a change in physical conditions, removal of toxic substances and concentration of the reactants at the surface of the clay. Changes in molecular configuration at the surface may also be important. Gottlieb & Simonoff (1952), Skinner (1956) and Pinck, Soulides & Allison (1961) have shown that adsorption of antibiotics by clays enables much more rapid bacterial growth to occur in culture media. The stimulation of nitrogen fixation by *Azotobacter* after addition of soil colloids or montmorillonite (McCalla, 1939; Macura & Pavel, 1959) has also been attributed to this process.

The significance of the concentration of nutrients at clay surfaces in relation to their uptake by microorganisms and plants has been widely discussed (Jenny & Overstreet, 1939; Dikusar, 1940; Zobell, 1943), although it is still not established. Many bacteria form a close association with colloidal particles (cf. references given by Estermann & McLaren, 1959) and this contact may be important in relation to nutrient uptake. The electron micrographs presented by Jenny & Grossenbacher (1963) show that an adsorption of the mucigel of plant roots by colloidal particles can occur.

The question of the removal of toxins by adsorption is important not only in relation to those generated in the soil by organisms, but also in relation to materials added to the soil, notably

insecticides, fungicides and herbicides This subject has been reviewed by Bailey & White (1964). Their discussion shows that those materials which have relatively small, non-polymeric molecules, and those which are negatively charged are not extensively adsorbed by clay minerals in presence of water. The detailed results obtained by Frissel (1961) support this observation particularly well. Frissel showed that the amounts of the herbicides he studied adsorbed by montmorillonite, illite and kaolinite from aqueous solution were very much less than sufficient to form a monolayer. In contrast, positively charged organic materials can be expected to be strongly adsorbed. Although a qualitative appreciation of some of the factors involved in adsorption can be obtained from a knowledge of the chemical constitution of the organic compound, Frissel concluded that "the quantities adsorbed are mainly determined by specific interaction forces of, *a priori*, unknown magnitude". Whenever the amount of adsorption is small in relation to the total available surface, determination of the mechanisms involved is very difficult, since the sites of adsorption may be non-characteristic of the surface. Competition for such sites with natural organic materials must occur, and the natural materials usually have the advantage of initial possession. However, the amounts of toxins applied are generally very small in relation to the weight of soil and except in the surface horizons competition with other organic compounds may not be important. Thus in spite of the small amount adsorbed per unit area of adsorbent, all the applied toxin may become attached to soil colloids. Because of the possibility of the gradual accumulation of adsorbed toxins, and the maintenance of small amounts in the soil solution in equilibrium with

these, the question of the type of secondary sites involved in specific interactions with organic compounds merits much further study.

Conclusions.

In most soils a large proportion of the organic material reacts with the inorganic colloids to form the clay-organic complex, and this reaction exerts an important influence on the physical, chemical and biological properties of the soil. The physical properties of clay-organic complexes indicate that the organic materials tend to be distributed around clay domains, rather than spread uniformly over the surfaces of clay particles. Although some understanding of the interaction between clays and defined organic compounds has now been obtained, an appreciation of the mechanisms responsible for the formation of the natural clay-organic complex is hindered by an inadequate knowledge of the structure and composition of soil organic compounds. On present knowledge it seems probable that adsorption of humic materials takes place predominantly through ionic linkages involving polyvalent cations or oxides as intermediates between the humic material and clay particle, whereas adsorption of polysaccharides is primarily due to physical adsorption forces. Drying and perhaps simple ageing of organic materials around clay materials may lead to the formation of films which can only be removed by drastic treatments. These hypotheses can only be substantiated by much further work with soil organic materials. The importance of polymer size, shape and charge characteristics suggests that much more work on these properties of soil organic compounds could profitably be undertaken.

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